THE PHYSICAL STRUCTURE OF BROWN COAL

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## Introduction

The behaviour of coal during processing is determined by its physicochemical composition and structure. The examination of the coal "molecule" has been hampered by the inability to find techniques which measure any meaningful properties of such large complex structures. Most attacks on the problem have been by means of breaking down the structure into smaller, more tractable pieces, examining these and inferring the original structure. With bituminous coals the severity of the treatment needed to rupture the molecules raises doubts as to the validity of the method. There is uncertainty even with brown coals which are geologically younger and bear more resemblance to the molecules of classical organic chemistry. This is reflected, for instance, in the diversity of models proposed for basic molecular arrangement (1-5).

Brown coals have the advantage that they can be broken down by the comparatively gentle treatment of alkali digestion (6) into fragments in the micron and submicron range. This results in a soluble fraction of humic acids and an insoluble residue, humins. With Victorian coals it has been found that maximum digestion occurs at pH 13 to give humic acid yields ranging from 15 to 40% of the dry coal mass (7).

This paper reports on a study of digested coal fractions which were subjected to particle size analysis using sedimentation techniques. For the humins fractions a gravitational sedimentation technique was adopted while the more finely divided humic acids required an ultracentrifuge to generate a sufficiently large force field. The nature of the fragments generated by this technique has resulted in a modified hypothesis of coal genesis.

## Experimental

The coal examined was a sample of medium-light earthy coal from the Yallourn mine in the Latrobe Valley, Victoria. Its ultimate analysis on a d.a.f. basis was C 65.6%, H 5.18% and oxygen by differnece 27.95%. A stock sample was prepared by wet ball milling, followed by further size reduction in a domestic food pulper and was then stored under water in a closed vessel.

For each test a 15 ml quantity of slurry was mixed with 500 ml quantity of 0.1 M NaOH solution to maintain pH at 13. After digesting overnight the slurry was wet-screened on a B.S. 350 mesh screen to remove +43 μm oversize particles. The under-flow was then passed through a micropore filter of nominal pore size 1.2 μm. The coal thus been fractionated by particle size into humins (the +43 μm and the -43 μm $_+$ 1.2 μm fractions) and humic acids (-1.2 μm fraction).

Some of each of the fractions was acid washed to remove sodium and reprecipitate the humic acids. A yellow supernatant liquid remained after precipitation of the humic acids, due to small quantities of fulvic acid. An elemental analysis was then carried out on the dried solids of each fraction.

Other samples of alkaline slurry were subjected to particle size analysis by sedimentation. With the -43 μm + 1.2 μm fraction this was done in a 50 mm diameter settling column with a tared pan at the base to continuously record the mass of sedimented solid. The data was analysed by the method of Odén (8) and the particle size distribution (Stokesian diameter) expressed on a mass % basis was calculated.

The humic acid fraction (-1.2 μm) which was a dark brown suspension containing 4.7 mg/l of coal did not settle even after standing for six months. This slurry was

spun in a Beckmann ultracentrifuge with special long tubes to generate high g values. Alkali-resistant polyallomer tubes were used so that the solids which collected in the base could be removed in a special guillotine, then dried and weighed. The heights of suspension charged varied from 10 to 80 mm and rotational speeds up to 40 000 rpm were used. The data was again analysed by Odén's method, modified according to Brown (9).

## Results

A typical output from the sedimentation balance for -43 µm +1.2 µm material so shown in Fig. 1. The occurence of distinct peaks indicates that groups of closely-sized particles are present, the smallest being about 6 µm in effective (Stokesian) diameter. The persistant appearance of the same size groups in all tests at different pH and with different coal types suggested that some fundamental unit was present. A microscopic examination of the material revealed that cylindrical rods about 0.9 µm in diameter and 6-8 µm long were common. When the drag coefficient for such particles was calculated from Lamb's formula for cylinders at low Reynolds' number (see Prandtl (10)), the terminal setting velocity was the same as for a spherical particle of about 6 µm diameter.

The larger particle sizes could thus be accretions of these basic units and a number is such agglomerations were noted. The rods were arranged side by side, close packed in bundles. It appears that the alkali peels these rods from the coal mass and they subsequently agglomerate in solution, doubling in volume at each coalescence.

Elemental analyses of the fractions showed the 'rod' fraction (-43 µm + 1.2 µm) is rich in both hydrogen and carbon compared with the original coal, Fig. 2 although the effect is partly obscured by the oxidation which takes place in alkaline solution. The same trends appeared in all coal samples tested.

The particle size distribution for the humic acid fraction is depicted in Fig. 3. No material sedimented out until the most extreme conditions were applied (40 000 rpm for 24 h), when some lightening of colour at the top of the solution was observed. The sedimented particles had a Stokesian diameter of around 2 nm, which means that a particle size gap of three orders of magnitude exists between these and the next largest particles detected (5 µm). Taking the density of coal substance to be 1.43 $g/cm^3$, a solid sphere of diameter 2 nm would have a molecular mass of 4,000. If the molecules were rod-shaped, even smaller molecular masses would be predicted. Literature values of the molecular mass of regenerated humic acids range between 800 and 20 000 with the values clustering around 1,000 and 10,000 (11,12,13).

Since the humic acid fraction constitutes 30% of the dry coal mass, about one third of the coal is in the form of small macromolecules, and bound to the coal structure with bonds weak enough to be disrupted by dilute alkali.

It is of interest to note that the particle size gap supplies a rational basis to the traditional German classification scheme of defining humic acid and humins on the basis of a particle size separation (filtration).

## Discussion

The presence of geometrically uniform rods and the absence of particles over such a wide particle size range have implications for our understanding of coal chemistry and genesis. The following discussion attempts to harmonise these observations.

Three explanations have been considered to explain the rods found during this work. These are that they are:-
    i) bacterial remains
    ii) plant cell remains
    iii) artifacts formed during phase separation in the coalification process.
Since bacteria, including rod-like bacilli are active during the biological digestion

stage of coalification, remnants of their protoplasm may have been incorporated
into the coal matrix. If this were so, their protein content should result in a
high nitrogen content and the results are listed in Table 1.

TABLE 1.
Nitrogen content (d.a.f.) of Coal Size Fraction

| Material | original coal | +43 μm | −43μm+1.2μm | −1.2 μm |
|---|---|---|---|---|
| Nitrogen content (% daf) | 0.75 | 0.63 | 0.78 | 0.70 |

Although the nitrogen content of the rod fraction is higher than the others,
it can only be significant if the rods constitute less than about 2% of the total
mass of the −43 μm + 1.2 μm fraction. Since their concentration appears to be much
greater than this, the hypothesis is unattractive.

The abundance of identifiable cell fragments observed under the microscope
lends weight to the second hypothesis. Cell sizes vary with location in the plant
and remains of coniferous tracheids or other cells would be of the correct size.
The composition of the rod fraction is close to that of lignin and the rods have
been observed peeling off larger woody fragments. The cell remains explanation
must therefore be considered as a possibility in the absence of other information.

The third hypothesis is more speculative and far-reaching in its implications.
It is generally accepted (14) that the first step in the genesis of coal is the
destruction of cellulose and the degradation of lignin to monomer which either is a
humic acid or polymerises to give humic acids. The polymerisation of these acids
takes place by condensation as indicated by the decrease in acidity with increase in
molecular mass. As the concentration of monomer decreases, a gel point is reached
and a giant network is formed, swollen by the solvent water. As the polymerisation
proceeds further, the network will become cross-linked, resulting in shrinkage and
water exclusion.

Considering macromolecules in surface energy terms, the solubility parameter
has been defined as

$$\delta = \left[\frac{E}{V}\right]^{\frac{1}{2}}$$

where E is the molar cohesive energy and V is the molar volume. For two polymers
A and B, the materials are compatible if (15),

$$(\delta_A - \delta_B)^2 < 4.2 \text{ kJ/l}$$

If this inequality does not hold phase separation of polymers will occur. The
solubility parameter of coal over a wide range of coal ranks has been measured
(15,17,18) and is plotted in Fig. 4. The value of δ falls nearly linearly from 32
to 23 as the carbon content rises from 70 to 89% and rises slowly thereafter. At
89% carbon, polar groups are largely absent and aromatisation has commenced. By
extrapolation back to the 65 −70% carbon range occupied by brown coals, the line is
steep enough such that a difference of only 1% in carbon content is sufficient to
create incompatibility between coal molecules.

A large polymer molecule is able to exist with different parts of the chain
in different phases and an increase in the concentration of the species will
concentrate solvated parts together as well as concentrating the precipitated parts.
With two different polymers e.g. polystyrene and polybutadiene blocks of one will
form within a continuous phase of the other, with domain sizes between 10 and 100 nm
usual. This segregation into phases will be enhanced by the swelling effect of the
remaining polymer.

In the case of coal formation, woody residues intermingle with condensation
polymers which are swollen by the water-soluble products from the degradation of

cellulose and lignin. The local changes in carbon content brought about by condensation polymerisation may be sufficiently large for phase separation to occur and the rods may be formed from local high-carbon regions, compare Fig. 2. Rod-shaped inclusions are known to form in materials like polyethylene oxide/poly-propylene oxide copolymers within certain concentration limits as listed below.

| high concentration of A | spheres of B dispersed in A |
| | rods " " " " " |
| ↓ | alternate layers of A and B |
| | rods of A disperesed in B |
| low concentration of A | spheres " " " " |

In this view rods are precipitates formed from the humic acid groundmass and represent a further step in the coalification chain.

The revised model of coal structure which emerges from this study envisages a gel of humic acid molecules swollen by water and incorporating particulates. These include rods and detrital matter like pollen, cell remains, exinite material etc. which are held together by the humic acid "glue". The bonds linking this mass together must be of a homopolar non-regenerable type as rheological studies of Victorian coals have shown that the bonds are broken by shear action during mechanical working and do not remake on standing (19). This excludes the hydrogen bond commonly regarded as the major bond type for brown coal gels, as hydrogen bonds are known to remake after rupture. It appears that van der Waals type bonds may hold the structure together. On rupture the water which is liberated on shearing would be able to attach at the vacant sites and thus prevent the remaking of the original stronger bonds.

Conclusions

1. Particle size analysis of alkali-digested brown coal provides a useful insight into coal structure.
2. Victorian coals contain significant quantities of cylindrical rod-shaped particles, 1 μm in diameter and 6-8 μm long, which are high in carbon and hydrogen.
3. No particles exist in alkali-digested coal solutions between 6 μm and 2mm Stokesian diameter.
4. Brown coal can be regarded as a gel of humic acids which incorporates larger particles bound by non-regenerable bonds.

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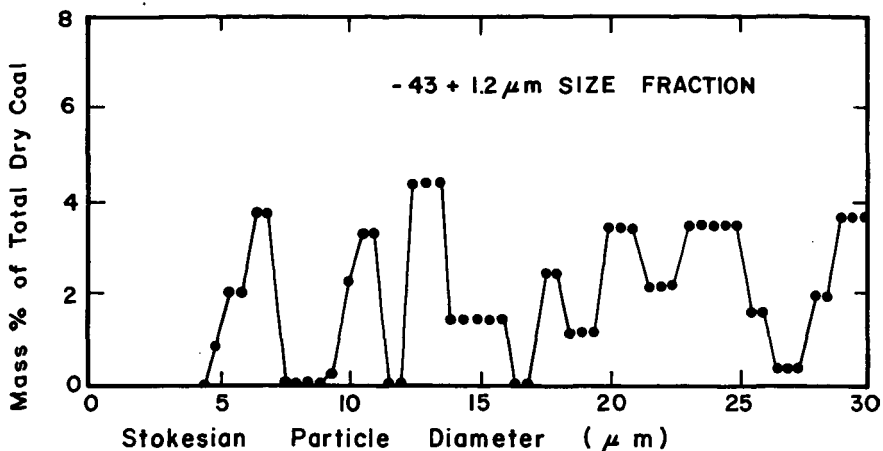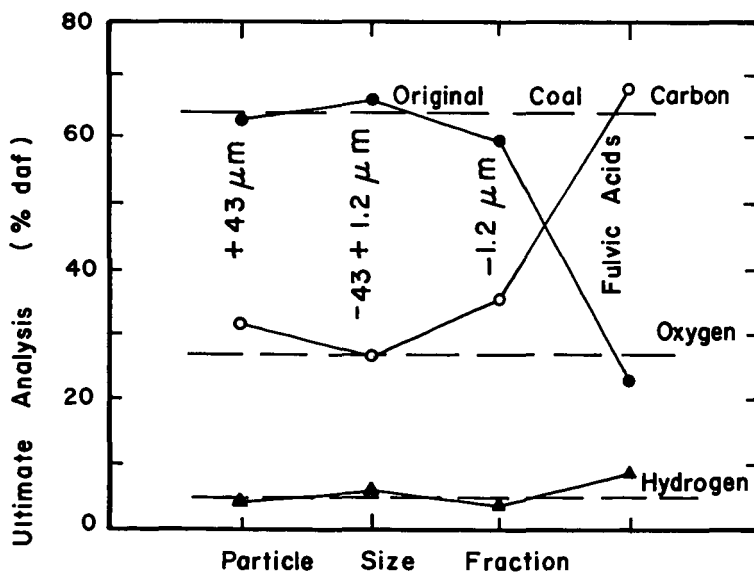
FIG. 1    PARTICLE   SIZE   DISTRIBUTION



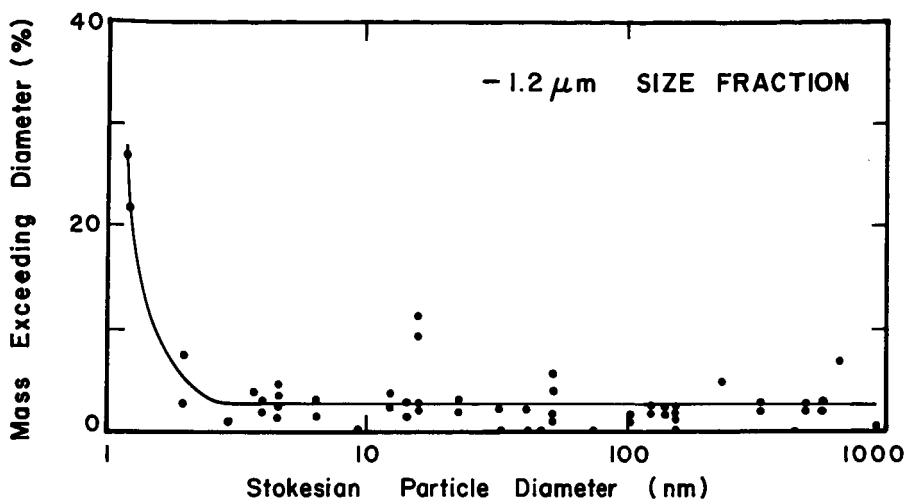FIG. 2    ULTIMATE   ANALYSIS   OF   FRACTIONS
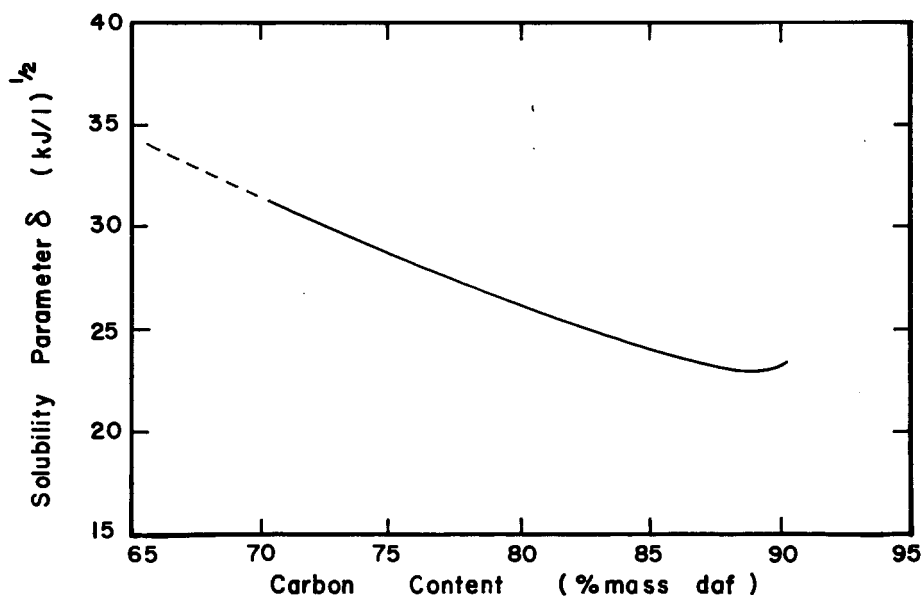
**FIG. 3    PARTICLE    SIZE    DISTRIBUTION**



**FIG. 4  SOLUBILITY    PARAMETER  vs    % CARBON**